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METHOD FOR PRODUCING CAPROLACTAM

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Patent Holder:	The right to use this patent belongs to the State under Act 34/1957 Zb., §3, paragraph 6.

The invention relates to a method for producing caprolactam from waste consisting of a mixture of polycaprolactam and a nonpolyamide component. Such waste materials arise during the processing of old tires containing polycaprolactam cords, for example, during the manufacture and processing of filled or laminated polycaprolactam, in the manufacture and processing of textiles from mixed fibers, and elsewhere. They cannot be incinerated, and several of the materials require special

decontamination procedure. The invention solves the problem of utilizing such wastes in an economically efficient way, and the goal of the invention is to allow them to be processed commercially into a high-quality, valuable product.

The nonpolyamide component of the waste materials, which are not water-soluble, differs depending on the origin of the waste. The nonpolyamide component cannot be separated from the polycaprolactam by mechanical grinding and classification.

Because of the chemical nature of the nonpolyamide component, or because of the high proportion it constitutes in the waste, the wastes are not suitable for utilization by known methods for treating wastes consisting solely of polycaprolactam. When direct thermal depolymerization to caprolactam is used, large quantities of residue remain in the reactor, and the resulting product is contaminated by the breakdown products of the nonpolyamide component; in the case of thermal depolymerization by steam, only dilute solutions of polycaprolactam are obtained. Considering the high energy requirements and the low yields of caprolactam, direct depolymerization is not economically efficient.

A method for dissolving polyamide in sulfuric acid was developed for utilizing waste resulting from regeneration of old tires. After the solution is filtered, the polycaprolactam was obtained by precipitating it out with water; the precipitate was dried and polycaprolactam was obtained in the form of a powder. This powder is used for molding applied coatings or is converted to granulated form. Wastes of other origins also can be processed to a polycaprolactam powder using polycaprolactam solvents other than sulfuric acid. A disadvantage of all these

approaches is the unsatisfactory quality of the powdered polycaprolactam obtained, which results from the degradation processes that operate during the dissolution of the polycaprolactam and from the impossibility of washing the precipitate completely clean. The resulting powder always has a lower molecular weight than the original polycaprolactam and always contains undesirable admixtures. On standing, it rapidly turns brown and forms a crumbly coating that adheres poorly to substrates. When melted, it produces a brownish granular material and items molded from it or fibers spun from it are of inferior quality.

It has now been found that such waste materials can be utilized economically for processing into a high-quality product by the method according to the invention, namely, by first dissolving waste mixtures of polycaprolactam and a nonpolyamide component in water or a polycaprolactam solvent. Dissolution in water is accomplished under elevated pressure at the melting point of polycaprolactam. According to alternative versions of the invention, all known polycaprolactam solvents can be used. Dissolution is accomplished at ordinary or elevated temperature depending on the type of solvent used. If the required temperature is above the boiling point of the solvent, the dissolution is accomplished under elevated pressure. Dissolution can be accomplished at ordinary temperatures when sulfuric acid, hydrochloric acid, phosphoric acid, formic acid, acetic acid, tricresol, or other solvents that dissolve polycaprolactam at ordinary temperatures are used. Dissolution can be accomplished at elevated temperatures without excess pressure with ethylene glycol, glycerin, dimethyl sulfoxide, methanolic or ethanolic

solutions of resorcinol, or calcium chloride or other solvents that dissolve polycaprolactam at temperatures higher than the temperatures but lower than their boiling points. Dissolution can also be accomplished at elevated temperatures without excess pressure using caprolactam, phenol, or other solvents that dissolve polycaprolactam at temperatures above their melting points but below their boiling points.

Dissolution can be accomplished at elevated pressure and elevated temperature with methanol, ethanol, or other solvents that dissolve polycaprolactam at temperatures above their boiling points. Dissolution can also be accomplished using suitable mixtures of solvents.

The nonpolyamide component is separated from the resulting polycaprolactam solution by filtering it through a suitable filtering device, preferably located in the bottom of the dissolution vessel. The type of filtering device depends on the particle size of the nonpolyamide component. It could be a perforated bottom or a wire screen, for instance. The nonpolyamide component retained by the filter is removed mechanically or by rinsing it off with the solvent used for the dissolution, and can be utilized further in some way depending on its nature. For example, particles of rubber or fiberglass can be used in construction as thermal insulation.

The polycaprolactam, in the form of a solution or suspension, is sent either directly or following removal of the solvent to thermal decomposition.

A suspension of polycaprolactam forms spontaneously on cooling, or on cooling accompanied by the loss of excess pressure when water or polycaprolactam was used for the dissolution.

These solvents do not introduce any chemically foreign substances into the depolymerization process, and the actual depolymerization process can also be accomplished in their presence. The process can also be accomplished, however, with these solvents being regenerated in the first phase by distillation. The suspension may also appropriately be conveyed directly to the depolymerization step when methanol or ethanol was used as the solvent, since these solvents also can be regenerated easily by distillation in the first phase of the depolymerization process.

If an organic or inorganic acid was used as the solvent, the polycaprolactam must first be isolated from the solution by precipitating it out with water or alcohol and separating it from the liquid phase by sedimentation, filtration, or centrifugation before it is sent on to be depolymerized. Since the waste acids in the liquid phase can be regenerated or decontaminated only with difficulty, the use of organic or inorganic acids as solvents is less desirable.

If ethylene glycol, glycerin, or dimethyl sulfoxide was used as the solvent, they can be removed from the resulting suspension by centrifugation, filtration, evaporation, extraction, or by another known means, and the polycaprolactam is then sent to thermal decomposition. The regenerated solvent can be reused in the dissolution step.

The thermal decomposition of polycaprolactam is accomplished by known methods, appropriately employing catalysts and superheated steam. The charge can consist of polycaprolactam obtained by the method described alone, or polycaprolactam in a mixture with other wastes of unfilled polycaprolactam. The

depolymerized product can be processed alone or together with the main stream of ordinary caprolactam produced by known methods to give the final product.

The advantage of the invention consists in the more economical utilization of waste relative to known methods in the form of powdered polyamide, since in conjunction with depolymerization, the method according to the invention can produce high-quality caprolactam, thus allowing for the utilization of polyamide waste on the commercial scale.

The subject matter of the invention is illustrated but not limited by the following examples:

Example 1

1 kg of waste from the production of polyamide laminate consisting of 70% polycaprolactam and 30% fiberglass was heated with 10 kg of water in an autoclave fitted with a metal screen. At 320°C the pressure in the autoclave was 23 kPa/cm². After one hour the resulting melt was discharged to a depolymerization reactor heated to 275°C. 2.5 g of H₃PO₄ and 2.5 g of H₃BO₃ were added to the melt as a mixed depolymerization catalyst, and the resulting monomeric caprolactam was distilled with steam superheated to 400°C. A 17% aqueous solution of caprolactam was obtained. After being condensed to a 92% solution it was cooled to 10°C and yielded 480 g of caprolactam and 170 g of mother liquor. A one-step distillation gave a final caprolactam with a

permanganate number of 6700 sec and volatile bases equivalent to 0.1 mL of 0.01N H_2SO_4 per 100 g of caprolactam. The mother liquor was recycled back to caprolactam production.

Example 2

1 kg of waste from the processing of old tires consisting of 60% polycaprolactam cord and 40% rubber was heated with 10 kg of ethylene glycol in a dissolving vessel with an outlet fitted with a metal screen. After being heated for six hours at $180^\circ C$, the resulting solution was discharged to a cooling vessel; after the solution had cooled to $60^\circ C$, polycaprolactam spontaneously precipitated out, forming a fine suspension. 8.3 kg of ethylene glycol were recovered from this suspension on a centrifuge, and polycaprolactam was isolated in the form of a fine paste which, after being washed with water, was conveyed to a depolymerization reactor. 3 g of H_3BO_3 were added to the paste as a depolymerization catalyst, and the temperature was gradually raised to $275^\circ C$. The resulting monomeric caprolactam was distilled with steam superheated to $400^\circ C$. An 18.5% aqueous solution of caprolactam was obtained. This was mixed with a 1% addition of activated carbon for adsorption [of impurities]. After the adsorbent was completely removed, the aqueous solution was condensed to 65% caprolactam and extracted three times with trichloroethylene. The caprolactam was extracted from the trichloroethylene into water and the aqueous extract was vacuum condensed and vacuum distilled with an addition of 0.5% NaOH. The yield was 34 g of the first fractions, 32 g of the last

fractions, and 416 g of final caprolactam. The final caprolactam had a permanganate number of 16,800 sec and contained volatile bases equivalent to 0.80 mL of 0.01N H_2SO_4 per 100 g of caprolactam.

Example 3

1 kg of textile waste consisting of 53% polycaprolactam fiber and 47% cotton fiber was heated with 10 kg of methanol at 130°C and a simultaneous pressure of 8.8 kPa/cm² in an autoclave in which the outlet was fitted with a metal screen. After one hour the resulting solution was discharged to a depolymerization reactor, where polycaprolactam spontaneously precipitated out and 6.7 kg of methanol spontaneously distilled off. As the resulting suspension of polycaprolactam was heated gradually to 275°C, 3.2 kg of methanol were distilled from it. To the polycaprolactam melt there were then added 5 g of H_3PO_4 as a depolymerization catalyst, and the resulting monomeric caprolactam was distilled with steam superheated to 400°C. The yield was a 15% aqueous solution of caprolactam that was condensed to give a concentration of 65% caprolactam, which was then extracted three times with trichloroethylene. After the caprolactam had been extracted from the trichloroethylene into water, the aqueous extract was vacuum condensed and vacuum distilled with an addition of 0.5% NaOH. The yield was 20 g of the first fractions, 20 g of the last fractions, and 390 g of

final caprolactam. The final caprolactam had a permanganate number of 10,590 sec and contained volatile bases equivalent to 1.20 mL of 0.01N H_2SO_4 per 100 g of caprolactam.

Claims

1. A method for obtaining caprolactam from waste mixtures of polycaprolactam and a nonpolyamide component, characterized in that wastes are brought into contact with water or a polycaprolactam solvent, with the dissolved caprolactam being separated from the nonpolyamide component and sent on, either directly or after preliminary removal of the solvent, to be thermally depolymerized, where monomeric caprolactam is regenerated, for example by steam.

2. A method as in Claim 1 characterized in that a solution of polycaprolactam in a solvent or a suspension of polycaprolactam in solvent is sent directly to be depolymerized, and the solvent is regenerated by distillation or is driven off with steam.

3. A method as in Claim 1 characterized in that the solvent is removed from the polycaprolactam, for example by centrifuging, filtration, extraction, or evaporation, prior to the depolymerization step.